

Novel Alkali and Alkaline Earth Hydrides for High Voltage and High Energy Density Batteries

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ABSTRACT

BlackLight Power, Inc. (BLP) of Cranbury, New Jersey, is developing a revolutionary technology based on novel hydrogen chemistry. More explicitly, energy is catalytically released as the electrons of atomic hydrogen are induced to undergo transitions to lower energy levels corresponding to fractional quantum numbers with the production of plasma, light, and novel hydrogen compounds (1-35). The Company uses a chemically generated or assisted plasma to form atomic hydrogen and a catalyst which react through a nonradiative energy transfer to form lower-energy hydrogen atoms called hydrinos. Since hydrinos have energy levels much lower than uncatalyzed hydrogen atoms, the energy release is intermediate between chemical and nuclear energies. The net enthalpy released may be over several hundred times that of combustion. Thus, the catalysis of atomic hydrogen represents a new source of energy with H_2O as the source of hydrogen fuel obtained by diverting a fraction of the output energy of the process to split water into its elemental constituents. Moreover, rather than air pollutants or radioactive waste, the products are novel compounds having hydride ions with increased binding energies that may be the basis of a high voltage battery. Such a high voltage battery would have the advantages of much greater power and much higher energy density where the limitations of battery chemistry attributed to the binding energy of the anion of the oxidant are addressed. The concept of our novel hydride battery and some preliminary results will be discussed during the presentation.

THEORY AND INTRODUCTION

J. J. Balmer showed in 1885 that the frequencies for some of the lines observed in the emission spectrum of atomic hydrogen could be expressed with a completely empirical relationship. This approach was later extended by J. R. Rydberg, who showed that all of the spectral lines of atomic hydrogen were given by the equation:

$$\bar{\nu} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (1)$$

where

$$R = 109,677 \text{ cm}^{-1}, n_f = 1, 2, 3, \dots, n_i = 2, 3, 4, \dots, \text{ and } n_i > n_f.$$

Niels Bohr, in 1913, developed a theory for atomic hydrogen that gave the energy levels in agreement with Rydberg's equation. An identical equation, based on a totally different theory for the hydrogen atom, was developed by E. Schrödinger, and independently by W. Heisenberg, in 1926.

$$E_n = -\frac{e^2}{n^2 8 \pi \epsilon_0 a_H} = -\frac{13.598 \text{ eV}}{n^2} \quad (2a)$$

$$n = 1, 2, 3, \dots \quad (2b)$$

where a_H is the Bohr radius for the hydrogen atom (52.947 pm), e is the magnitude of the charge of the electron, and ϵ_0 is the vacuum permittivity.

The excited energy states of atomic hydrogen are given by Eq. (2a) for $n > 1$ in Eq. (2b). The $n = 1$ state is the "ground" state for "pure" photon transitions (the $n = 1$ state can absorb a photon and go to an excited electronic state, but it cannot release a photon and go to a lower-energy electronic state). However, an electron transition from the ground state to a lower-energy state may be possible by a nonradiative energy transfer such as multipole coupling or a resonant collision mechanism. Processes such as hydrogen molecular bond formation that occur without photons and that require collisions are common (36). Also, some commercial phosphors are based on resonant nonradiative energy transfer involving multipole coupling (37).

We propose that atomic hydrogen may undergo a catalytic reaction with certain atomized elements and ions which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, $m \cdot 27.2 \text{ eV}$ wherein m is an integer. The theory and supporting data was given previously (1-35). The reaction involves a nonradiative energy transfer to form a hydrogen atom that is lower in energy than unreacted atomic hydrogen that corresponds to a fractional principal quantum number. That is

$$n = \frac{1}{2} \cdot \frac{1}{3} \cdot \frac{1}{4} \cdots \frac{1}{p}; p \text{ is an integer} \quad (2c)$$

replaces the well known parameter $n = \text{integer}$ in the Rydberg equation for hydrogen excited states. The $n=1$ state of hydrogen and the $n = \frac{1}{\text{integer}}$ states of hydrogen are nonradiative, but a transition between two nonradiative states

is possible via a nonradiative energy transfer, say $n = 1$ to $n = 1/2$. In these cases, during the transition the electron couples to another electron transition, electron transfer reaction, or inelastic scattering reaction which can absorb the exact amount of energy that must be removed from the hydrogen atom to cause the transition. Thus, a catalyst provides a net positive enthalpy of reaction of $m \cdot 27.2 \text{ eV}$ (i.e. it absorbs $m \cdot 27.2 \text{ eV}$ where m is an integer). Certain atoms or ions serve as catalysts which resonantly accept the nonradiative energy transfer from hydrogen atoms and release the energy to the surroundings to affect electronic transitions to fractional quantum energy levels. As a consequence of the nonradiative energy transfer, the hydrogen atom becomes unstable and emits further energy until it achieves a lower-energy nonradiative state having a principal energy level given by Eqs. (2a) and (2c).

EXPERIMENTAL OBSERVATIONS

A number of independent experimental observations lead to the conclusion that atomic hydrogen can exist in fractional quantum states that are at lower energies than the traditional "ground" ($n = 1$) state. Prior related studies that support the possibility of a novel reaction of atomic hydrogen which produces a chemically generated or assisted plasma (rt-plasma) and produces novel hydride compounds include extreme ultraviolet (EUV) spectroscopy (6-9, 11-15, 17, 18, 21-23), characteristic emission from catalysis and the hydride ion products (9-13), lower-energy hydrogen emission (4, 6, 7-8, 17), plasma formation (9, 11-13, 21-22, 24-25), Balmer α line broadening (7, 9, 14, 15, 17-19), elevated electron temperature (7, 18), anomalous plasma afterglow duration (24, 25), power generation (7, 9, 14-17, 19-21, 32), and analysis of chemical compounds (26-32). Exemplary studies include:

1) the observation of intense extreme ultraviolet (EUV) emission at low temperatures (e.g. $\approx 10^3 \text{ K}$) from atomic hydrogen and only those atomized elements or gaseous ions which provide a net enthalpy of reaction of approximately $m \cdot 27.2 \text{ eV}$ via the ionization of t electrons to a continuum energy level where t and m are each an integer (e.g. K , Cs , and Sr atoms and Rb^+ ion ionize at integer multiples of the potential energy of atomic hydrogen and caused emission; whereas, the chemically similar atoms, Na , Mg , and Ba , do not ionize at integer multiples of the potential energy of atomic hydrogen and caused no emission) (9, 11-13, 21, 22, 24, 25),

2) the observation of novel EUV emission lines from microwave and glow discharges of helium with 2% hydrogen with energies of $q \cdot 13.6 \text{ eV}$ where $q = 1, 2, 3, 4, 6, 7, 8, 9, 11, 12$ or these lines inelastically scattered by helium atoms in the excitation of $He(1s^2)$ to $He(1s^1 2p^1)$ that were identified as hydrogen transitions to electronic energy levels below the "ground" state corresponding to fractional quantum numbers as shown in Figure A(6, 7, 17),

3) the observation of novel EUV emission lines from microwave and glow discharges of helium with 2% hydrogen at 44.2 nm and 40.5 nm with energies of

$$q \cdot 13.6 + \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \cdot 13.6 \text{ eV} \quad \text{where } q = 2 \quad \text{and}$$

$n_f = 2, 4$ $n_i = \infty$ that corresponded to multipole coupling to give two photon emission from a continuum excited state atom and an atom undergoing fractional Rydberg state transition (7),

4) the identification of transitions of atomic hydrogen to lower energy levels corresponding to lower-energy hydrogen atoms in the extreme ultraviolet emission spectrum from interstellar medium and the sun (1, 4, 6, 8),

5) the EUV spectroscopic observation of lines by the Institut für Niedertemperatur-Plasmaphysik e.V. that could be assigned to transitions of atomic hydrogen to lower energy levels corresponding to fractional principal quantum numbers and the emission from the excitation of the corresponding hydride ions (23),

6) the recent analysis of mobility and spectroscopy data of individual electrons in liquid helium which shows direct experimental confirmation that electrons may have fractional principal quantum energy levels (5),

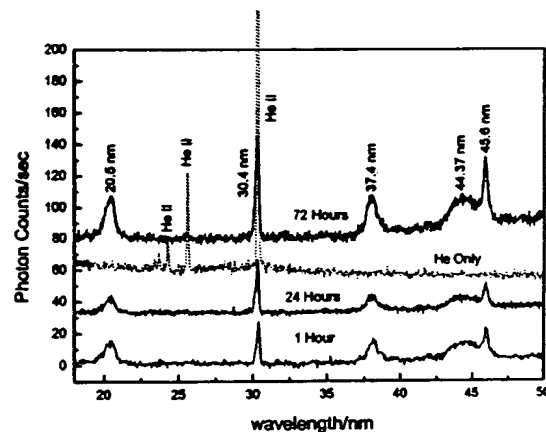


Figure A. The EUV spectra (15-50 nm) of the microwave cell emission of the helium-hydrogen mixture (98/2%) recorded at 1, 24, and 72 hours with a normal incidence EUV spectrometer and a CEM, and control helium (dotted curve) recorded with a 4° grazing incidence EUV spectrometer and a CEM. The pressure was maintained at 20 torr. Only known He I and He II peaks were observed with the helium control. Reproducible novel emission lines that increased with time were observed at 45.6 nm and 30.4 nm with energies of $q \cdot 13.6 \text{ eV}$ where $q = 2$ or 3 and at 37.4 nm and 20.5 nm with energies of $q \cdot 13.6 \text{ eV}$ where $q = 4$ or 6 that were inelastically scattered by helium atoms wherein 21.2 eV (58.4 nm) was absorbed in the excitation of $He(1s^2)$.

7) the observation of novel EUV emission lines from microwave discharges of argon or helium with 10% hydrogen that matched those predicted for vibrational transitions of $H_2^+[n=1/4; n^*=2]^+$ with energies of $\nu \cdot 1.185 \text{ eV}$, $\nu = 17 \text{ to } 38$ that terminated at the predicted dissociation limit, E_D , of $H_2^+[n=1/4]^+$, $E_D = 42.88 \text{ eV}$ (28.92 nm) (8),

8) the observation of continuum state emission of Cs^{2+} and Ar^{2+} at 53.3 nm and 45.6 nm, respectively, with the absence of the other corresponding Rydberg series of lines from these species which confirmed the resonant nonradiative energy transfer of 27.2 eV from atomic hydrogen to the catalysts atomic Cs or Ar^+ (13),

9) the spectroscopic observation of the predicted hydride ion $H^-(1/2)$ of hydrogen catalysis by either Cs atom or Ar^+ catalyst at 407 nm corresponding to its predicted binding energy of 3.05 eV (13),

10) the observation of characteristic emission from K^{3+} which confirmed the resonant nonradiative energy transfer of 3-27.2 eV from atomic hydrogen to atomic K (12),

11) the spectroscopic observation of the predicted $H^-(1/4)$ ion of hydrogen catalysis by K catalyst at 110 nm corresponding to its predicted binding energy of 11.2 eV (12),

12) the observation of characteristic emission from Rb^{2+} which confirmed the resonant nonradiative energy transfer of 27.2 eV from atomic hydrogen to Rb^+ (11),

13) the spectroscopic observation of the predicted $H^-(1/2)$ ion of hydrogen catalysis by Rb^+ catalyst at 407 nm corresponding to its predicted binding energy of 3.05 eV (11),

14) the observation by the Institut für Niedertemperatur-Plasmaphysik e.V. of an anomalous plasma and plasma afterglow duration formed with hydrogen-potassium mixtures (24),

15) the observation of anomalous afterglow durations of plasmas formed by catalysts providing a net enthalpy of reaction within thermal energies of $m \cdot 27.28 \text{ eV}$ (24, 25),

16) the observation of Lyman series in the EUV that represents an energy release about 10 times that of hydrogen combustion which is greater than that of any possible known possible chemical reaction (9, 11-13, 21, 22, 24, 25),

17) the observation of line emission by the Institut für Niedertemperatur-Plasmaphysik e.V. with a 4° grazing incidence EUV spectrometer that was 100 times more energetic than the combustion of hydrogen (23),

18) the observation of anomalous plasmas formed with Sr and Ar^+ catalysts at 1% of the theoretical or prior known voltage requirement with a light output per unit power input up to 8600 times that of the control standard light source (14, 15, 20, 21),

19) the observation that the optically measured output power of gas cells for power supplied to the glow discharge increased

by over two orders of magnitude depending on the presence of less than 1% partial pressure of certain catalysts in hydrogen gas or argon-hydrogen gas mixtures, and an excess thermal balance of 42 W was measured for the 97% argon and 3% hydrogen mixture versus argon plasma alone (20),

20) the observation that glow discharge plasmas of the catalyst-hydrogen mixtures of strontium-hydrogen, helium-hydrogen, argon-hydrogen, strontium-helium-hydrogen, and strontium-argon-hydrogen showed significant Balmer α line broadening corresponding to an average hydrogen atom temperature of 25-45 eV; whereas, plasmas of the noncatalyst-hydrogen mixtures of pure hydrogen, krypton-hydrogen, xenon-hydrogen, and magnesium-hydrogen showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 3 \text{ eV}$ (17-19),

21) the observation that microwave helium-hydrogen and argon-hydrogen plasmas having catalyst Ar^+ or He^{2+} showed extraordinary Balmer α line broadening due to hydrogen catalysis corresponding to an average hydrogen atom temperature of 110-130 eV and 180-210 eV, respectively; whereas, plasmas of pure hydrogen, neon-hydrogen, krypton-hydrogen, and xenon-hydrogen showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 3 \text{ eV}$ (7, 18),

22) the observation that microwave helium-hydrogen and argon-hydrogen plasmas showed average electron temperatures that were high, 28,000 K and 11,600 K, respectively; whereas, the corresponding temperatures of helium and argon alone were only 6800 K and 4800 K, respectively (7, 18),

23) the observation of significant Balmer α line broadening of 17, 9, 11, 14, and 24 eV from rt-plasmas of incandescently heated hydrogen with K^+/K^+ , Rb^+ , cesium, strontium, and strontium with Ar^+ catalysts, respectively, wherein the results could not be explained by Stark or thermal broadening or electric field acceleration of charged species since the measured field of the incandescent heater was extremely weak, 1 V/cm, corresponding to a broadening of much less than 1 eV (9),

24) calorimetric measurement of excess power of 20 mW/cc on rt-plasmas formed by heating hydrogen with K^+/K^+ and Ar^+ as catalysts (9),

25) the high resolution visible spectroscopic observation from rt-plasma and plasma electrolysis cells of the predicted $H^-(1/2)$ ion of hydrogen catalysis by each of K^+/K^+ , Rb^+ , Cs, and Ar^+ at 407 nm corresponding to its predicted binding energy of 3.05 eV as shown in Figure B(9, 10),

26) the isolation of novel inorganic hydride compounds such as $KHKHCO_3$ and KH following each of the electrolysis and plasma electrolysis of a K_2CO_3 electrolyte which comprised high binding energy hydride ions that were stable in water with their identification by methods such as (i)

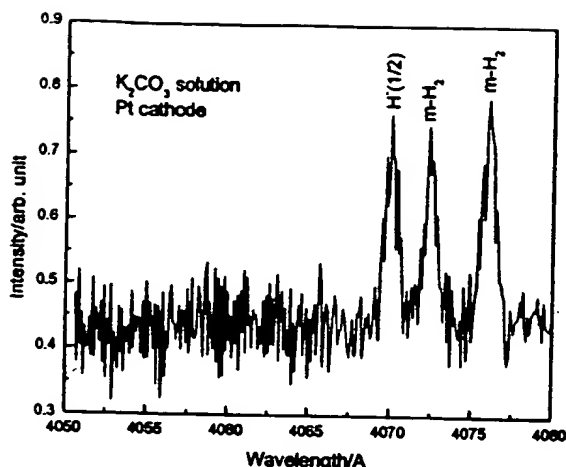


Figure B1. The high resolution visible spectrum in the region of 407 nm recorded on the emission of K_2CO_3 plasma electrolysis cell.

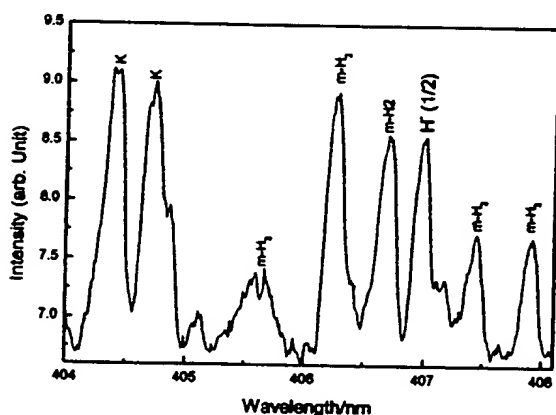


Figure B2. The high resolution visible spectrum in the region of 407 nm recorded on the emission of the rt-plasma formed by atomic hydrogen and gaseous potassium ion catalyst generated by a filament heater. In both cases, the novel 407.0 nm peak which could not be assigned to a known peak was assigned to $H^-(1/2)$.

ToF-SIMS on $KHKHCO_3$, which showed inorganic hydride clusters $K[KHKHCO_3]^+$ and a negative ToF-SIMS dominated by hydride ion, (ii) X-ray photoelectron spectroscopy which showed novel peaks corresponding to high binding energy hydride ions, and (iii) proton nuclear magnetic resonance spectroscopy which showed upfield shifted peaks corresponding to more diamagnetic, high-binding-energy hydride ions (10, 28, 29, 31),

27) the observation that the power output exceeded the power supplied to a hydrogen glow discharge plasmas by 35-184 W depending on the presence of catalysts helium or argon and less than 1% partial pressure of strontium metal in noble gas-hydrogen mixtures; whereas, the chemically similar noncatalyst krypton had no effect on the power balance (19),

28) the Calvet calorimetry measurement of an energy balance of over $-151,000 \text{ kJ/mole } H_2$ with the addition of 3% hydrogen to a plasma of argon having the catalyst Ar^+ compared to the enthalpy of combustion of hydrogen of $-241.8 \text{ kJ/mole } H_2$; whereas, under identical conditions no change in the Calvet voltage was observed when hydrogen was added to a plasma of noncatalyst krypton (16),

29) the observation that upon the addition of 10% hydrogen to a helium microwave plasma maintained with a constant microwave input power of 40 W, the thermal output power was measured to be at least 400 W corresponding to a reactor temperature rise from room temperature to 1200 °C within 150 seconds, a power density of 40 MW/m^3 , and an energy balance of at least $-5 \times 10^5 \text{ kJ/mole } H_2$ compared to the enthalpy of combustion of hydrogen of $-241.8 \text{ kJ/mole } H_2$ (17),

30) the differential scanning calorimetry (DSC) measurement of minimum heats of formation of KHI by the catalytic reaction of K with atomic hydrogen and KI that were over $-2000 \text{ kJ/mole } H_2$ compared to the enthalpy of combustion of hydrogen of $-241.8 \text{ kJ/mole } H_2$ (32),

31) the isolation of novel hydrogen compounds as products of the reaction of atomic hydrogen with atoms and ions which formed an anomalous plasma as reported in the EUV studies (26-32),

32) the identification of novel hydride compounds by a number of analytic methods as such as (i) time of flight secondary ion mass spectroscopy which showed a dominant hydride ion in the negative ion spectrum, (ii) X-ray photoelectron spectroscopy which showed novel hydride peaks and significant shifts of the core levels of the primary elements bound to the novel hydride ions, (iii) 1H nuclear magnetic resonance spectroscopy (NMR) which showed extraordinary upfield chemical shifts compared to the NMR of the corresponding ordinary hydrides, and iv) thermal decomposition with analysis by gas chromatography, and mass spectroscopy which identified the compounds as hydrides (26-32),

33) the NMR identification of novel hydride compounds MH^*X wherein M is the alkali or alkaline earth metal, X , is a halide, and H^* comprises a novel high binding energy hydride ion identified by a large distinct upfield resonance as shown in Figure C (26-31),

34) the replication of the NMR results of the identification of novel hydride compounds by large distinct upfield resonances at Spectral Data Services, University of Massachusetts Amherst, University of Delaware, Grace Davison, and National Research Council of Canada (26),

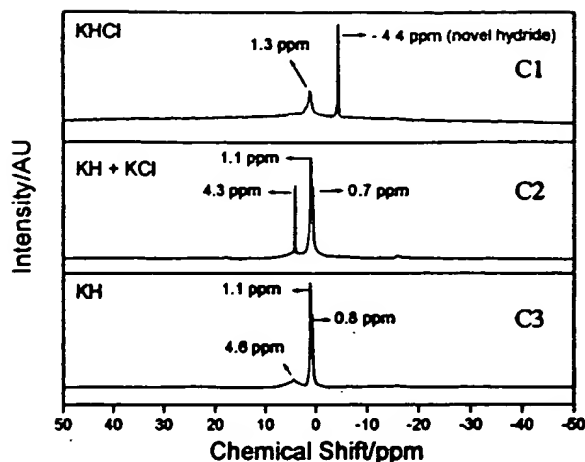


Figure C. (1) The ^1H MAS NMR spectrum of KH^*Cl relative to external tetramethylsilane (TMS). The resonance at 1.3 ppm was assigned to ordinary hydride ion. The large distinct upfield resonance at -4.4 identifies a hydride ion with a substantially smaller radius as compared with ordinary hydride since a smaller radius increases the shielding or diamagnetism, and it was assigned to a novel hydride ion of KH^*Cl . (2) The ^1H MAS NMR spectrum of the control comprising an equal molar mixture of KH and KCl relative to external tetramethylsilane (TMS). Ordinary hydride ion has a resonance at 1.1 ppm and 0.8 ppm in the KH/KCl mixture and in KH . The presence of KCl does not shift the resonance of ordinary hydride as shown in Figure C3. (3) The ^1H MAS NMR spectrum of the control KH relative to external tetramethylsilane (TMS).

35) the NMR identification of novel hydride compounds MH^* and MH_2^* wherein M is the alkali or alkaline earth metal and H^* comprises a novel high binding energy hydride ion identified by a large distinct upfield resonance that proves the hydride ion is different from the hydride ion of the corresponding known compound of the same composition (26).

HYDRIDE ION BATTERY

Hydride ions formed by the catalysis of atomic hydrogen having extraordinary binding energies may stabilize a cation M^{*+} in an extraordinarily high oxidation state such as +2 in the case of lithium. Thus, these hydride ions may be used as the basis of a high voltage battery of a rocking chair design wherein the hydride ion moves back and forth between the cathode and anode half cells during discharge and charge cycles. Exemplary reactions for a cation M^{*+} are shown in Figure D.

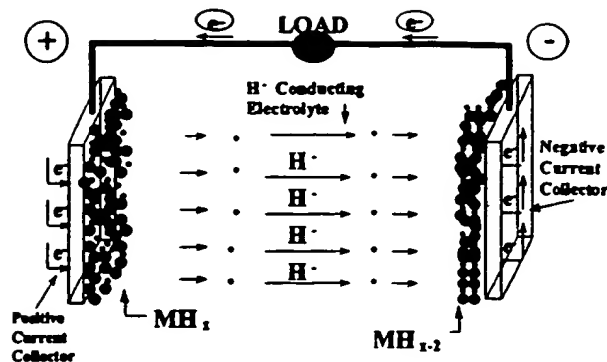
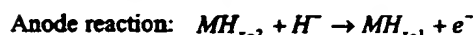


Figure D. The schematic of a hydride ion battery comprising the reactions for a cation M^{*+} of:



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